

## Periodic Boundary Quantum Chemical Study on ZnO Ultra-Violet Laser Emitting Materials

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### 1. Introduction

Recently ZnO has attracted much attention in the ultraviolet laser emitting devices since Koinuma et al.[1-2] reported the construction of ZnO films on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) surface using laser molecular beam epitaxy techniques and observed an ultraviolet laser emission of the above material as pumped by YAG laser. These films were deposited on  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>(0001) substrates by laser molecular beam epitaxy (laser MBE) resulting in c-axis oriented heteroepitaxy. The films were composed of hexagonally shaped nanocrystals which had coalesced into a honey-comb like structure. The optical properties of the film were very sensitive to the crystal quality and the size of nanocrystals. To control these factors, it is highly important to understand the heteroepitaxy mechanism involved in such a large lattice mismatch system. The crystal structure of ZnO is wurtzite and the stacking sequence of atomic layers along the c-axis is not symmetric. A crystal with c-axis normal to the surface, as determined by X-ray diffraction, can be either [0001] or [000 $\bar{1}$ ] oriented, depending on whether the (0001) Zn face or the (000 $\bar{1}$ ) O face forms the terminating layer. These two crystallographic planes are known to exhibit different physical and chemical properties. However, the significance of the terminating atomic layer has hardly been discussed for heteroepitaxial ZnO thin films. Most of the work on this topic have been carried out experimentally and theoretical reports are lacking.

Another important subject in the field of semiconductors is the fabrication of double heterostructure (DH) composed of a thin well layer sandwiched between two barrier layers which has been utilized in lasers diode to facilitate radiative recombination by carrier confinement[3]. The bandgap engineering is one of the challenging problems in the fabrication of a DH laser diode using a ZnO active layer. Modulation of the bandgap keeping the lattice constants similar is essential for this purpose. In the present study, we therefore concentrate on the surface structure, polarity and bandgap of ZnO.

### 2. Computational Details

The calculations have been carried out using periodic density functional method. The surface structure and polarity of ZnO have been calculated using DSolid code within Kohn-Sham formalism. The one electron Schrödinger equation was solved only at  $k=0$  wavevector point of the Brillouin zone.

The Vosko-Wilk-Nusair local-type functional was used for geometry optimization. The double numerical set plus polarization functions (DNP) basis set was used which allows great vibrational freedom.

The changes in the bandgap and structural properties of bulk ZnO structure on doping various metals were also calculated using CASTEP code within Kohn-Sham formalism. Here the one electron Schrödinger equation was solved at 7 wavevector points of the Brillouin zone. The local density approximation (Perdew-Zunger parametrization) or spin-polarized version of Perdew-Zunger parametrization was used for geometry optimization. The basis set used is the plane-wave with pseudo potential and the cut off value for plane-wave is 900 eV which allowed accurate energy calculation.

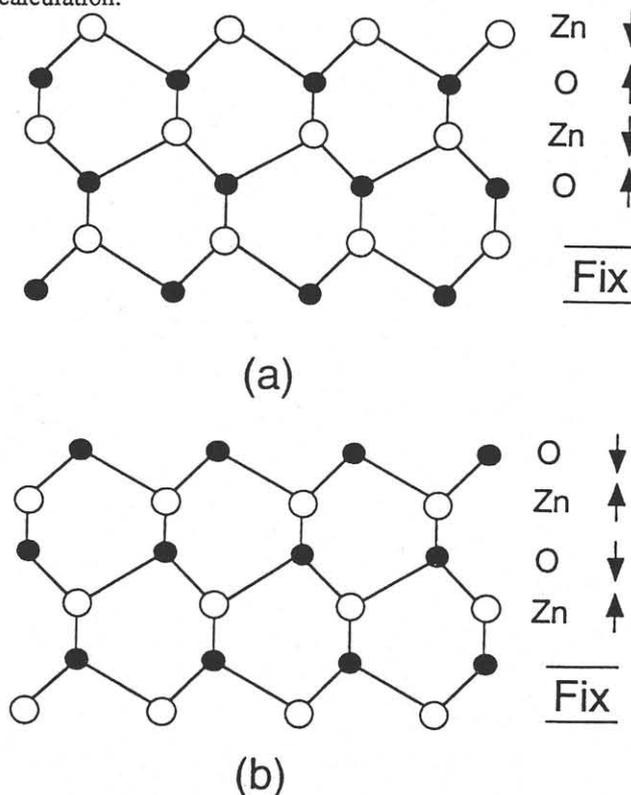


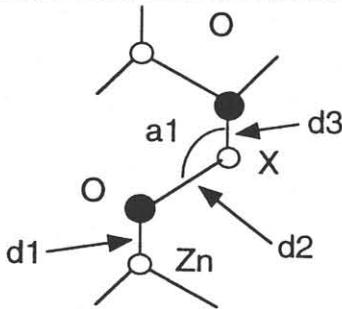
Fig. 1. The surface models of ZnO (a) [0001] Zn surface (b) [000 $\bar{1}$ ] O surface

### 3. Results and Discussion

The surface models of ZnO are shown in Fig.1. The bottom layer was fixed and only the top two layers were allowed to move during optimization. The Zn and O layers move in the opposite directions and in both cases the top layer moves down and the next layer moves up during optimization. This kind of movement is called rumpling. The optimized structures of both [0001] Zn and [000 $\bar{1}$ ] O surfaces are found to be similar. The vertical distance between the plane of first and second layers are calculated as 0.29 Å for [0001] Zn surface, 0.31 Å for the [000 $\bar{1}$ ] O surface and it is 0.81 Å in the ZnO bulk. This shows that the layers are very close at the surface. The calculated surface relaxation energies for these two surfaces reveal that the [000 $\bar{1}$ ] O surface is more stable than the [0001] Zn surface by 6 kcal/mol. This is in very good agreement with the experimental identification that the growth direction of ZnO films are with [000 $\bar{1}$ ] surface[4]. The charge distribution analysis on these two models shows that [0001] Zn surface is ionic and [000 $\bar{1}$ ] O surface is relatively covalent. In the former the HOMO and LUMO are localized on both Zn and O atoms while in the latter, HOMO is localized on the Zn-O bonds and LUMO is expanded on the surface.

Table I Bandgap and Selected Parameters of the Optimized Structures of Zn<sub>1</sub>X<sub>1</sub>O<sub>2</sub>

Species (X)	Bandgap (eV)	a1 [deg]	d1 [Å]	d2 [Å]	d3 [Å]	ion radius[Å]
Zn	0.83	107.8	2.02	2.01	2.02	0.74
Be	1.90	107.0	1.99	1.78	1.53	0.41
Mg	1.67	106.5	2.02	1.98	1.98	0.71
Pd	0.10	118.7	2.06	2.15	2.26	0.78
Co	0.26	113.0	2.02	1.99	1.96	0.79
Ni	0.18	111.3	2.00	1.99	1.98	0.83
Ca	1.37	109.5	1.96	2.15	2.26	1.14
Sr	1.50	111.1	1.95	2.20	2.34	1.32



The band energy calculations for the occupied orbitals were carried out using 7 k-points of the Brillouin zone. The values of  $\alpha$ ,  $\beta$  and  $\gamma$  were fixed and the other cell parameters were optimized. To obtain the complete band structure of ZnO the calculations were carried out including the unoccupied orbitals also. The modulation of bandgap of ZnO has been done by doping various metals and the structural properties have been calculated. The ZnO supercell is represented as Zn<sub>1</sub>X<sub>1</sub>O<sub>2</sub> where X=Be, Mg, Pd, Co, Ni, Ca, Sr and Zn. The bandgaps and the optimized structures for ZnO doped with various metals are presented in Table 1. The band gap is found to increase on doping of Be, Mg, Ca and

Sr whereas it decreases with Co, Ni and Pd. This shows that the IIA group metals are preferable to increase the bandgap of ZnO. Among these four metals which increase the bandgap of ZnO, only Mg is found to have an ionic radii similar to that of Zn. A wide band gap and greater stability are observed for the structure Zn<sub>1</sub>Mg<sub>1</sub>O<sub>2</sub>. The c/a value decreases with the increase in strength of ionic bond and this value of Mg is found to be similar to that of Zn compared to the other metals (Fig. 2).

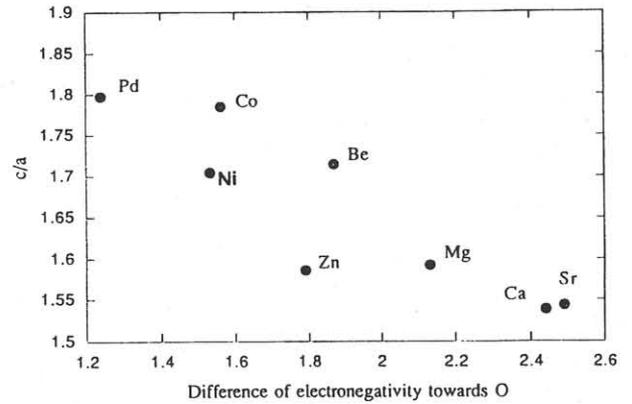


Fig. 2. Correlation of c/a with ion tendency

To retain the wurtzite structure, the c/a ratio should be in a particular range and the above graph shows that this value is closer to Zn only in the case of Mg and the other ions have either lower or higher values. Though a much wider bandgap is obtained by doping Be than Mg, Be can not form a stable structure as its ionic radius is very small and the c/a value is large compared to Zn. This results reveal that only Mg doped ZnO can form a stable layer with wide bandgap and similar lattice constants as that of ZnO. This agrees very well with the experimental reports[5].

### 4. Conclusions

The surface structure, polarity and bandgap of ZnO were studied using periodic density functional method. The calculations reveal that [000 $\bar{1}$ ] O surface of ZnO is more stable than the [0001] Zn surface; the latter is ionic in nature while the former surface is relatively covalent. The modulation of the bandgap of ZnO was carried out by doping various metals and the wide bandgap with greater stability is observed for the structure Zn<sub>1</sub>Mg<sub>1</sub>O<sub>2</sub>.

### References

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